Supporting Information for the communication entitled:

Pore Size Dependent Dynamics of Confined Water Probed by FIR Spectroscopy

by

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1. Description of the organic monomers

We have synthesized a wide range of homologues by changing the number and nature of selected atoms in appendages and studied their structural influence in the solid state crystalline structures. Several of these compounds were considered promising candidates to give hollow tubular structures, whereas other molecules were chosen to probe the structural requirements in detail. Of the homologues studied that include flexible linear appendages (Chart 1, Supplementary Information), six are hydrated: $(\pm)7\cdot 2H_2O-(\pm)12\cdot 2H_2O$, forming the required isomorphic porous structures. These six crystalline systems constitute a unique group of iso-structural pores with identical threedimensional hydrogen-bond networks (Figure 1, Supplementary Information). The main differences between these structures can be attributed to the length of the monomer appendages, which affect the inner size of the pore by narrowing the diameter. From the group of homologues with restricted conformational movement due to their branched and cyclic appendages, only two, derived from interdigitated single-stranded head-totail chains, incorporate water molecules: $(\pm)24 \cdot H_2O$ and $(\pm)28 \cdot \frac{1}{2}H_2O$ (Chart 2, Supplementary Information). The rest of the compounds studied, including the homologues with oxygenated appendages (Chart 3, Supplementary Information), generated an anhydrous packing composed mostly of double-stranded head-to-tail arrays. These results prove that when structurally robust hydrogen-bonding patterns are employed, it is once more the combined steric requirements and the conformational flexibility of the appendages that govern which framework is adapted. We argue, at the same time, that the architecture of the target material can be reached by systematic changes in the size of monomers.

In this work, we have selected for our study the crystalline structures formed by molecules: 7, 11, 12, 17 (Chart 1, Supplementary Information) and 25, 28 (Chart 2, Supporting Information).



Figure 1. (A) Molecular structure of (\pm) **11**·2H₂O showing the structural H-bonded water molecule. (B) Macro-ring system showing the hydrogen bonds and the disorder of water molecules inside the pore.



Chart 1. Models with linear appendages



Chart 2. Models with branched and cyclic appendages

S2



Chart 3. Models with oxygenated appendages

S3

2. Analytical data of the reported compounds

Analytical data of compound (±)12·2H₂O

Synthetic experimental procedure and spectroscopic and physical data

Compound 12 was synthesized by condensing the dilithium salt of 3-methylenecyclohexanecarboxylic acid with hept-1-en-4-one following the synthetic sequence reported for other member of this family of compounds.² Single crystals of compound 12 suitable for X-ray analysis⁵ were grown at room temperature from a damp carbon tetrachloride/2,2,4-tetramethylpentane mixture (4:1), after several days.

(1*R**,5*R**,7*S**)-7-Allyl-5-hydroxymethyl-7-propyl-6-oxabicyclo[3.2.1]octane-1

carboxylic acid (12). Crystalline solid: mp 112 - 113 °C; R_f 0.70 (ethyl acetate); IR (CHCl₃) 3414 (br), 2963 (s), 2873 (m), 1702 (s), 1462 (w), 1264 (m), 1135 (w), 1044 (w), 913 (m), 733 (m) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 6.05-5.95 (m, 1H), 5.13 (d, J = 16.8 Hz, 1H), 5.08 (d, J = 9.2 Hz, 1H), 3.59 (d, J = 11.6 Hz, 1H), 3.48 (d, J = 11.6 Hz, 1H), 2.87 (br d, J = 12.0 Hz, 1H), 2.69 (br d, J = 7.2 Hz, 2H), 2.38-2.32 (m, 1H), 2.12-1.98 (m, 2H), 1.82-1.61 (m, 4H), 1.59-1.52 (m, 2H), 1.48 (d, J = 11.6 Hz, 1H), 1.40-1.27 (m, 1H), 0.88 (t, J = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 178.67, 134.70, 117.14, 86.72, 82.56, 66.64, 55.71, 40.30, 39.75, 37.00, 31.99, 31.12, 19.08, 16.84, 14.68. HRMS calcd for C₁₃H₁₉O₄ (M-C₂H₅)⁺ 227.1283, found 227.1272. Analysis: Calculated for C₁₅H₂₄O₄: C, 67.14; H, 9.01. Found: C, 67.12; H, 9.20.

Analytical data of compound (±)17

Synthetic experimental procedure and spectroscopic and physical data

Compound **17** was prepared by treatment of ethyl-5-hydroxymethyl-7-oxa-6-oxabicyclo [3.2.1] octan-1- carboxylate with 2.5 equiv of 3-butenyl magnesium bromide following the synthetic sequence reported for other unsaturated members of this family of compounds.³ Single crystals of compound **17** suitable for X-ray analysis⁵ were grown at room temperature from a damp carbon tetrachloride/dichloromethane (5:1) mixture, after several days.

(1R*,5R*)-7,7-Dibut-3-enyl-5-hydroxymethyl-6-oxabicyclo[3.2.1]octane-1-

carboxylic acid (17). Crystalline solid: mp 102.3-102.8 °C; R_f 0.64 (ethyl acetate); IR(KBr) 3357 (m), 3072 (m), 2955 (m), 1695 (s), 1642 (w), 1464 (w), 1401 (w), 1270

(m), 1177 (w), 1033 (s), 988 (w), 909 (s), 728 (m), 660 (w) cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 5.87-5.74 (m, 2H), 5.03 (br d, J = 17.2 Hz, 1H), 4.99 (br d, J = 17.2 Hz, 1H), 4.95 (br d, J = 10.2 Hz, 1H), 4.93 (br d, J = 10.2 Hz, 1H), 3.54 (d, J = 11.7 Hz, 1H), 3.43 (d, J = 11.7 Hz, 1H), 2.84 (ddd, J = 12.0, 2.6, 2.6 Hz, 1H), 2.31-2.22 (m, 2H), 2.17-1.85 (m, 6H), 1.79-1.57 (m, 5H), 1.45 (d, J = 12.0 Hz, 1H), 1.28 (br ddd, J = 12.0, 2.6, 7.0 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 178.7, 138.7, 138.5, 114.7, 114.3, 86.9, 82.5, 66.7, 55.8, 40.6, 36.2, 32.0, 31.2, 31.1, 28.9, 28.5, 19.1. HRMS calcd for C₁₇H₂₆O₄ M⁺ 294.1831, found 294.1847. Analysis: Calculated for C₁₇H₂₆O₄: C, 69.36; H, 8.90. Found: C, 69.40; H, 8.89.

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